Vacancy-phosphorus complexes in strained $Si_{1-x}Ge_x$: Structure and stability

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We have used positron annihilation spectroscopy to study vacancy-type defects in strained phosphorus doped $Si_{1-x}Ge_x$ layers grown on Si substrates and irradiated with 2-MeV protons. The results show that the dominant defect in the SiGe layer after irradiation is the *E* center, the vacancy-phosphorus pair. When the sample is annealed at 150–175 °C, the dominant defect species in the SiGe layer changes into a complex consisting of a vacancy, a phosphorus dopant, and a germanium atom (*V*-P-Ge complex). Furthermore, we observe that the total concentration of vacancy-type defect complexes before and after annealing remains approximately constant. We thus conclude that the *V*-P-Ge complex is formed when a migrating *E* center encounters a Ge atom and forms the *V*-P-Ge complex. The *V*-P-Ge complex anneals out at 200 °C. The 50 °C higher annealing temperature of the *V*-P-Ge complex corresponds to about 0.1–0.2 eV larger binding energy than that of the *V*-P pair. By *ab initio* calculations, we reproduce this value and confirm that the *V*-P pair is more stable when neighbored by a germanium atom.

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I. INTRODUCTION

Silicon-germanium (SiGe) has become the focus of numerous studies in recent years thanks to its promising properties in semiconductor technology. The complete solubility of the two elements enables band-gap engineering between the values of pure silicon and pure germanium. The improvement in device performance has made the incorporation of strained and relaxed SiGe, grown epitaxially on silicon substrates, into silicon based devices attractive.[1] However, the introduction of new technology seldom goes without delay, and reliability problems often accompany devices processed with a new technique. Some progress has been made concerning the misfit strain relaxation phenomena,[2] but bulk properties of both strained and relaxed SiGe, especially the formation of electrically active defect complexes, are not fully understood.

The understanding of the formation and migration of vacancy related defects in semiconductors is of fundamental importance for device fabrication. Vacancies and vacancy complexes can introduce energy levels in the forbidden band gap and act as compensating centers and charge carrier traps, which influence the electrical properties of the semiconductor. In silicon, the vacancy donor pair, the so-called *E* center, has been shown to play a significant role both for the electrical properties of the semiconductor and in the migration of impurities and dopants.[3] At dopant concentrations below 10^{20} cm^{-3}, vacancy assisted migration is the predominant migration mechanism for large dopant atoms in silicon, e. g. As and Sb.[3] In highly *n*-type silicon (dopant concentration $>10^{20}$ cm^{-3}), the diffusing *E* centers interact with each other or with other ionized donors which may lead to dramatic changes in diffusivities.[4,5]

Recently, some progress has been made in the study of defect formation and defect annealing in strained SiGe. Mamor *et al.* reported that the activation enthalpies of several deep-level defects decrease with increasing Ge content in *p*-type SiGe.[6] Monakhov *et al.* have reported on defect characteristic electronic levels in n-type strained proton irradiated SiGe[7,8] measured by deep-level transient spectroscopy (DLTS). These studies identify the dominating defect in irradiated SiGe as the vacancy phosphorus pair. However, the annealing and migration of the *E* center is not yet fully understood.

In this study, we use positron annihilation spectroscopy (PAS) in combination with computational methods to identify vacancy-type defects in proton irradiated strained SiGe layers. We confirm that the dominating defect in the as-irradiated samples is the so-called *E* center, consisting of a silicon vacancy and a phosphorus dopant (*V*-P). We also observe that this defect is mobile in the temperature interval 150–175 °C and by migration forms a new defect, the *V*-P-Ge complex, consisting of a silicon vacancy, a phosphorus dopant, and a germanium atom. The *V*-P-Ge complex is observed to anneal out above 200 °C.

Previous theoretical work by Boguslawski and Bernholc give that the formation energy of a vacancy in $Si_{0.5}Ge_{0.5}$ is lowered by 0.25 eV for each Ge atom surrounding the vacancy.[9] They attribute this to a energy difference in germanium and silicon dangling bonds around the vacancy. The qualitative description of the vacancy in SiGe is further developed in the framework of the Schlüter model in Ref. 10. Essentially, the orbital energy of the paired dangling bonds in the vacancy is lower when more delocalized Ge dangling bonds are involved.

We thus attribute the higher annealing temperature of the *V*-P-Ge to a Ge dangling bond. Our *ab initio* calculations for the binding of the *V*-P pair to a germanium atom show that

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TABLE I. The characteristics of the samples used in the study.

Ge content (%)	p^+ dose (cm^{-2})
4	
4	3×10^{14}
4	6×10^{14}
4	1.6×10^{15}
7	
7	3×10^{14}
7	6×10^{14}

the V-P-Ge complex is about 0.1–0.2 eV more stable than the V-P pair, in good agreement with the experiment.

II. EXPERIMENT AND DATA ANALYSIS

A. Samples

The studied samples were epitaxial $Si_{1-x}Ge_x$ layers on Czochralski grown Si(100) substrates. The silicon substrate was weakly n-type (P doped $\sim10^{14}$ cm^{-3}). In order to obtain a clean deposition surface, the substrate was subjected to a H_2 atmosphere for 2 min prior to the deposition of the SiGe layer. The SiGe layer was grown with chemical vapor deposition and the layer thickness was 1 μm for all samples. Two germanium concentrations were used, 4% and 7%. The layers were grown n type with a P concentration of $\approx10^{18}$ cm^{-3}. In order to produce a homogeneous defect distribution within the SiGe layer, some of the samples were irradiated with 2-MeV protons. The proton dose varied between 3×10^{14} cm^{-2} and 1.6×10^{15} cm^{-2}. X-ray-diffraction measurements confirmed that the SiGe layers remained fully strained after deposition and irradiation. This was also the case for annealed samples. The characteristics of the samples are summarized in Table I.

B. Positron experiments

The vacancy-type defect distribution as well as the bulk properties of the strained SiGe layer were studied with a monoenergetic positron beam. Positron spectroscopy has been shown to be a versatile tool in the study of vacancy-type defects.[11,12] Positrons can either be taken directly from a β^+ source, as is done in the conventional lifetime and Doppler broadening measurements, or as in this case be moderated and then accelerated to a desired energy and implanted in the sample. This enables the study of defect distributions in thin layers and even defect profiling with the Doppler broadening technique.

After implantation, the positrons thermalize within a few picosecond and thereafter diffuse in the sample until they annihilate with electrons. Neutral and negative vacancy-type defects in the lattice can act as positron traps. When a positron is trapped by a vacancy its lifetime increases and the momentum distribution of the annihilating electron-positron pair narrows because of the reduced electron density.

The momentum of the annihilating positron-electron pair can be detected as Doppler broadening of the 511-keV annihilation line. For the measurement of the Doppler broadening, we used a Ge detector with an energy resolution of 1.3 keV at 511 keV. For the presentation of Doppler broadening measurements, it is customary to use the parameters S and W to describe the shape of the annihilation line. The low-momentum parameter S is the fraction of counts in the central part of the annihilation line and thus, it describes mainly annihilation with low momentum valence electrons. Correspondingly, W is the high-momentum parameter obtained as the fraction of counts in the wing region of the annihilation line describing annihilation mainly with core electrons. Consequently, an increase (decrease) in S (W) parameter indicates the presence of vacancy-type defects.

The measured S (W) parameter is a superposition of the S (W) parameter of the bulk and the parameters of the different defects in the sample. Near the surface, the annihilation of the positron at the surface also has to be accounted for. In the simplest case where the positrons only annihilate in two different states, the measured S and W parameters are given by

$$S=\eta_1 S_1+\eta_2 S_2, \tag{1}$$

$$W=\eta_1 W_1+\eta_2 W_2, \tag{2}$$

where η_1 and η_2 are the fraction of positrons annihilating in states 1 and 2, respectively. Consequently, $\eta_2=1-\eta_1$. From the equations above, it is evident that, in this case, the measured parameters form the segment of a line in the (S,W) plane between the two annihilation states (S_1,W_1) and (S_2,W_2). This fact can be useful for the identification of trapping centers.

For the high-momentum region of the annihilation line, the contribution of the momentum of the thermalized positron is negligible and the spectrum is dominated by the core electrons. This part of the annihilation line can therefore be used to identify the surroundings of the vacancy. In order to fully utilize the information in the high-momentum region, a coincidence measurement, where both annihilation photons are detected, is necessary, since much of the information is otherwise embedded in the background. We used a coincidence setup with two germanium detectors to study strained $Si_{1-x}Ge_x$ layers and to identify the vacancy-type defects in irradiated and annealed samples.

After initial measurements both unirradiated and irradiated samples were annealed *in situ*. All annealings were done in vacuum. In order to suppress positron diffusion to the surface and thus reduce surface annihilation within the native oxide, which otherwise influences the Doppler spectrum in the energy region 0–10 keV, the annealed samples were etched in HF acid. After etching the samples were immediately transferred to the vacuum chamber. Close attention was paid to the annihilation of positrons at the surface for annealed samples. No significant changes were observed in the surface Doppler parameters for samples annealed below 300 °C.

C. Theoretical core electron momentum distributions

It has previously been shown that calculations for positron annihilation both in bulk material and in vacancy-type defects can be a useful tool in combination with experiment for defect identification and characterization in semiconductors, see, e.g., Ref. 13. We have used the atomic superposition method within the conventional scheme (a localized positron does not affect the average electron density) in calculating the positron states. The annihilation rates with different electron states are obtained in the generalized gradient approximation (GGA) for the enhancement of the electron density at the positron. The momentum distribution of annihilating electron-positron pairs are obtained by superimposing contributions of individual electron states calculated in the independent particle model and weighted with the proper GGA annihilation rates. The calculated spectra are convoluted with experimental resolution before comparison. For the details of the scheme, see Ref. 14, and references therein. In the present work, also the valence electron contribution to the momentum distribution was taken into account within the same scheme. The defect calculations were performed using 216 atom supercells.

The calculations have been done for strained $Si_{1-x}Ge_x$ crystals. The lattice constant in the strained direction has been calculated from

$$a_{st}=\left[1-\sigma_{st}\left(\frac{a_S-a_L}{a_L}\right)\right]a_L, \tag{3}$$

where a_S is the lattice constant of the substrate (silicon) and a_L is the lattice constant of the relaxed $Si_{1-x}Ge_x$. The lattice constant in the relaxed SiGe has been calculated with Vegard's law, which has been shown to be a good approximation in SiGe.[15,16] The coefficient σ_{st} can be calculated from the strain tensor.

All calculations of positron annihilation characteristics have been done with the atoms on their respective lattice sites, i.e., no relaxation around a vacancy-type defect has been taken into account. By comparing measured and calculated results for the positron lifetime for the *E* center and the divacancy in silicon this has been proven to a good approximation. The calculations done in this study for the *E* center and the divacancy match previous results.[17]

III. VACANCY-PHOSPHORUS PAIRS AS POSITRON TRAPS IN IRRADIATED SiGe LAYERS

A. Introduction of vacancies vs fluence and positron annihilation states

In Fig. 1, we show the Doppler parameters *S* and *W* as a function of positron implantation energy for as-grown and as-irradiated samples. Also indicated in the figure is the mean positron implantation depth. As can be noted, the results for the as-grown samples (Ge content 4% and 7%) are almost identical and the SiGe layer cannot be clearly distinguished since the *S* and *W* parameters continuously approach the silicon substrate values with increasing positron implantation energy.

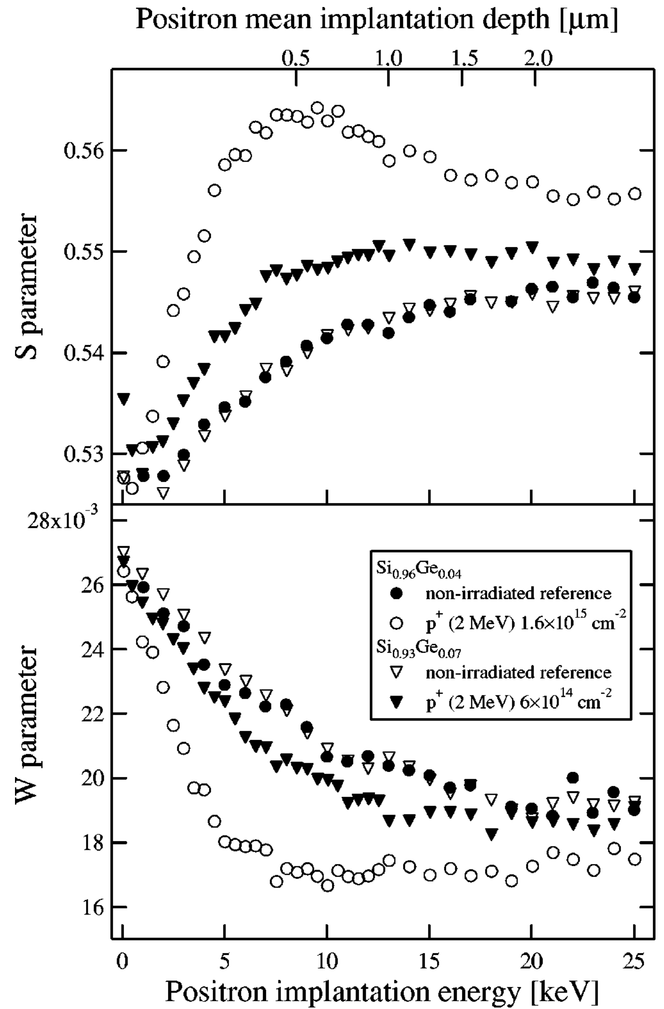

FIG. 1. *S* and *W* parameters as a function of positron implantation energy for as-deposited and as-irradiated samples. Indicated in the figure is also the mean implantation depth of the positrons.

For the samples implanted with a proton dose of 6×10^{14} cm^{-2}, the *S* and *W* parameters clearly differ from the nonirradiated samples. When the proton dose is further increased by a factor of ≈ 2, the changes in the *S* and *W* parameter curves are significant. For the sample with a Ge content of 4% and a proton dose of 1.6×10^{15} cm^{-2}, the $Si_{1-x}Ge_x$ layer can clearly be distinguished as a plateau in the *S* parameter curve in the energy interval ~5–12 keV. The large increase (decrease) in the *S* (*W*) parameter is an indication of the enhanced formation of vacancy defects in the SiGe layers.

Positron trapping into charged vacancy-type defects depends on temperature, whereas trapping into neutral defects is temperature independent.[11,12] This fact can be used to distinguish vacancy defects in the SiGe layers from vacancy defects in the substrate. In Fig. 2, we show the *S* parameters for the samples irradiated with a proton dose of 6×10^{14} cm^{-2} (a) and 1.6×10^{15} cm^{-2} (b) as a function of measurement temperature in the temperature interval 20–300 K. The two *S* parameter curves represent mainly annihilation in the $Si_{1-x}Ge_x$ layer (open symbols) and silicon substrate (full symbols), respectively. As can be seen from Fig. 2(a),

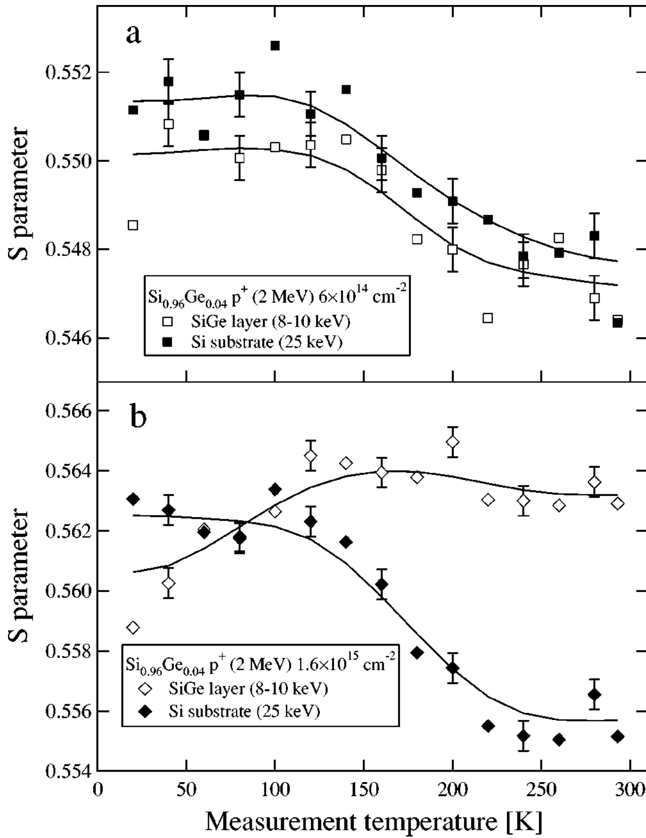

FIG. 2. S parameter values for $Si_{0.96}Ge_{0.04}$ samples irradiated with proton (2 MeV) doses 6×10^{14} cm^{-2} and 1.6×10^{15} cm^{-2} as a function of measurement temperature. The solid lines are guides to the eye.

the substrate S parameter increases with decreasing temperature, which is a fingerprint for negatively charged positron traps.[18] This behavior is also seen in the SiGe layer for this sample, indicating that the trapping center in the layer also is in a negative charge state. The S parameter in the layer irradiated with the higher dose [Fig. 2(b)] shows a completely different temperature behavior than the substrate, the S parameter is approximately constant between 100 and 300 K.

The vacancy-type defect that traps positrons is not expected to depend on irradiation dose nor is it expected to change charge state, since the samples are still n type. The temperature independent S parameter therefore indicates that all positrons annihilating in the highly doped SiGe layer get trapped at vacancies, i.e., we have saturation trapping. The weakly n-type substrate in this sample has a similar temperature behavior as the sample irradiated with a smaller fluence, i.e., no saturation trapping.

The (S,W) plot of the $Si_{0.96}Ge_{0.04}$ sample irradiated with 1.6×10^{15} cm^{-2} protons in Fig. 3 is divided into two distinct lines. When the positron implantation energy is between 0.1 and 10 keV, the data points fall on a line joining the surface to the defect state in the $Si_{0.96}Ge_{0.04}$ layer. At energies between 10 and 25 keV, they form a line from the defect state to the silicon substrate state. The sharp turning point between the two lines indicated in the figure is typical for saturation trapping, i.e., all positrons with this implantation energy annihilate in the defect state. This conclusion is the same as deduced from the measurement of the S parameter versus temperature (Fig. 2), where the S parameter stays constant over a large temperature interval. By comparing the turning point of the (S, W) plot with the known divacancy parameters in silicon[19,20] ($S_{V_2}/S_B=1.05$), which is indicated in the figure, it is evident that the (S,W) turning point in the $Si_{0.96}Ge_{0.04}$ layer is closer to the (S,W) bulk parameters than expected for a divacancy (or a bigger vacancy cluster). This enables us to identify the W and S parameters at the turning point as the characteristic parameter values for a monovacancy-type defect in the SiGe layer.

B. Identification of V-P complexes in SiGe

The saturated S parameter value for the SiGe layer in the sample irradiated with the highest dose (Figs. 1 and 3) is not high enough to enable it to be due to a divacancy or a bigger vacancy cluster. A complex consisting of a single monovacancy is therefore the only candidate. It is well established

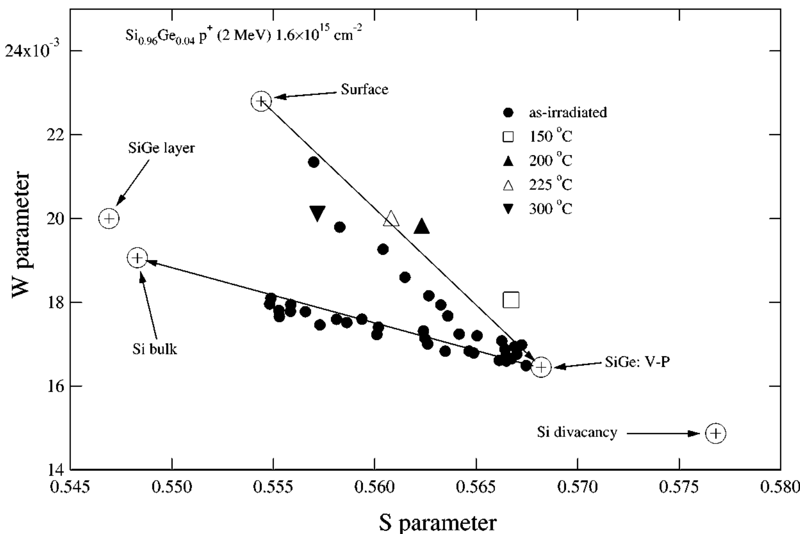

FIG. 3. S-W plot for the as-irradiated sample ($Si_{0.96}Ge_{0.04}$, proton dose 1.6×10^{15} cm^{-2}). Indicated in the figure are the characteristic (S, W) points of the measured SiGe layer, the Si bulk, the V-P pair, and the Si divacancy in the silicon substrate. The solid lines are solutions of Eqs. (1) and (2), where the annihilation states are the surface state and the V-P pair, and the Si bulk state and the V-P pair, respectively. The arrows indicate increasing positron implantation energy. The turning points after some of the isochronal annealings are also shown.

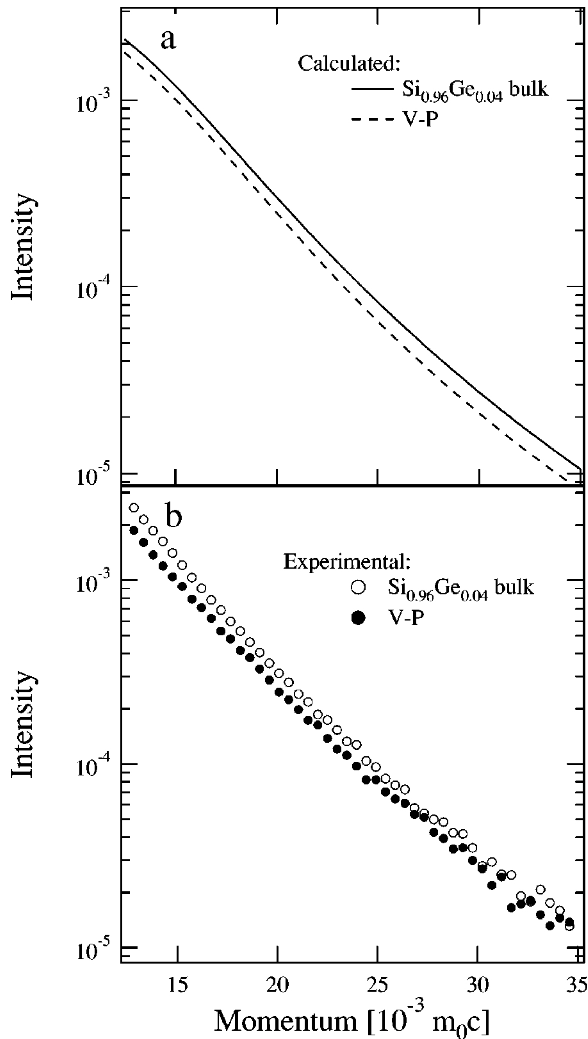

FIG. 4. (a): Calculated core electron momentum distributions for the $Si_{0.96}Ge_{0.04}$ bulk and for the V-P pair. The distributions have been convoluted with a Gaussian resolution function in order to mimic the experimental conditions. (b): Experimental core electron momentum distributions for the $Si_{0.96}Ge_{0.04}$ bulk and for the V-P pair.

that the monovacancy in n-type silicon is mobile below room temperature,[21] this is most likely also the case for the silicon monovacancy in SiGe containing only a small fraction of germanium. A consequence of the high mobility of the monovacancy in pure undoped silicon is that it anneals out below room temperature. However, monovacancy-impurity complexes are stable above room temperature in silicon. In moderately and highly n-type float-zone silicon,[22,23] the mobile monovacancies have a high probability to get trapped at phosphorus dopants. Due to the high dopant concentration, the vacancy phosphorus pair is therefore most likely the dominant defect also in the $Si_{1-x}Ge_x$ layer.

We therefore infer that the detected defect in the $Si_{0.96}Ge_{0.04}$ layer is the vacancy phosphorus (V-P) pair. The identification is confirmed by core electron momentum measurements with the coincidence technique of the sample irradiated with a proton dose of 1.6×10^{15} cm^{-2}. In Fig. 4, we present momentum distributions for the $Si_{0.96}Ge_{0.04}$ bulk and for the E center (V-P) together with corresponding calculated distributions. As can be seen, the shape of the experimental and calculated distributions match well. The decrease in intensity for the E-center momentum distribution, as well as the similarity in the shapes of the bulk and defect distributions is expected. The intensity in the high-momentum region for both the bulk and the E center is mainly due to $2p$ electrons, which are the outermost core electrons for both silicon ($Z_{Si}=14$) and phosphorus ($Z_P=15$). When a positron annihilates in the E center, the impact on the momentum distribution is just a reduction in intensity in the high-momentum region, due to the reduced overlap of the positron wave function with the core electrons. The shape of the momentum distribution is not changed. The agreement between the calculated and experimental W parameter values for the V-P pair in the as-irradiated samples is also good, as can be seen from Table II.

It can be noted that a small fraction of the vacancy-type defects in the SiGe layer could be situated next to a germanium atom and form a V-P-Ge complex. The random nature of the silicon germanium crystal restricts this amount to only 4% of the total V-P concentration, which is not enough to be detected.

TABLE II. Experimental (core electron momentum measurements with coincidence technique from the sample irradiated with a proton dose of 1.6×10^{15} cm^{-2}) and calculated W parameter values for strained $Si_{0.96}Ge_{0.04}$ layers. All values have been normalized to the SiGe bulk value. A typical error of W/W_B is 0.02. Full width at half maxmimum (FWHM) describes the resolution of the detector system.

	S/S_B $[0,3]\times10^{-3}$ m_0c	W/W_B $[15,20]\times10^{-3}$ m_0c	W/W_B $[20,25]\times10^{-3}$ m_0c	FWHM (keV)
Measurements				
$Si_{0.96}Ge_{0.04}$ as deposited	$S_B=0.576$	$W_B=0.003460$	$W_B=0.000918$	0.914
as irradiated	1.05	0.78	0.81	0.921
150 °C 50 min	1.05	0.89	0.95	0.924
150 °C 240 min+175 °C 60 min	1.04	0.98	1.04	0.922
150 °C 240 min+175 °C 270 min	1.04	1.02	1.08	0.920
Calculations				
Bulk		$W_B=0.003529$	$W_B=0.000911$	0.914
V-P		0.84	0.82	0.921
V-P-Ge		1.00	1.01	0.920

The identification of V-P pairs in the SiGe layer is consistent with the expected introduction rate and defect concentrations in the sample irradiated with 1.6×10^{15} cm^{-2} protons. Since positron trapping is in saturation in the SiGe layer, the concentration of V-P pairs is in the 10^{18} cm^{-3} range. This is expected for a primary defect concentration obtained with this proton fluence. Since the phosphorus concentration is high, the primary vacancies are efficiently captured by phosphorus dopants forming V-P pairs. On the other hand, the concentration of vacancy-type defects in the substrate of this sample is of the order of 10^{16} cm^{-3}, as expected for a secondary defect.[24] The dominating defect as observed by PAS in the weakly n-type as-irradiated substrate ($n\approx10^{14}$ cm^{-3}) is therefore most likely the divacancy. The enhancement of positron trapping at low temperatures (Fig. 2) shows that at least a fraction of the divacancies in the substrate are negatively charged.

IV. MIGRATION AND ANNEALING OF VACANCY PHOSPHORUS COMPLEXES

A. Changes of positron traps in thermal annealings

In order to study the recovery of the V-P pair, the sample with the highest vacancy concentration, irradiated with a proton dose of 1.6×10^{15} cm^{-2}, was isochronally annealed for 30 min in the temperature interval 100–450 °C. The measurements were done at room temperature. The S and W parameters vs. positron implantation energy after some of the annealings are shown in Fig. 5. Significant changes in the W parameter curves start to appear after annealing in 150 °C, for the S parameter the changes become significant when the temperature is raised to 200 °C. When the temperature is further increased, the S and W vs energy curves gradually approach the bulk values, indicating that the vacancy complexes anneal out. Above 350 °C, no vacancy-type defects are observed.

After annealing at 150 °C, only a small change in the S parameter curve can be seen. However, the changes in the W parameter curve is significant. This trend is also seen in the turning points of the annealed samples which have been included in the (S, W) plot of Fig. 3. The sharp turning point in the S-W plane is an indication that the positrons still experience saturation trapping, i.e., all positrons annihilate in a defect in the SiGe layer. Furthermore, if one examines the turning points in this temperature interval more closely, it seems that the W parameter for the turning points is slightly above the line connecting the defect and the surface state. This suggests that a new defect, with a higher characteristic W parameter, is formed in this temperature interval.

To characterize this defect more accurately, isothermal annealings were carried out on the sample irradiated with a proton dose of 1.6×10^{15} cm^{-2}. The sample was first subjected to annealing at 150 °C for a total of 230 min, after this the sample was further annealed at 175 °C for a total of 270 min. The change in the W parameter value at the turning point of the (S,W) plot is shown as a function of annealing time in Fig. 6. As can be seen the W parameter increases continuously from the characteristic V-P value until it saturates after ≈300 min of annealing. The increase in the W parameter as a result of annealing is due to an increase in the positron annihilation probability with core electrons. After 300 min of annealing no significant change in the W parameter is seen.

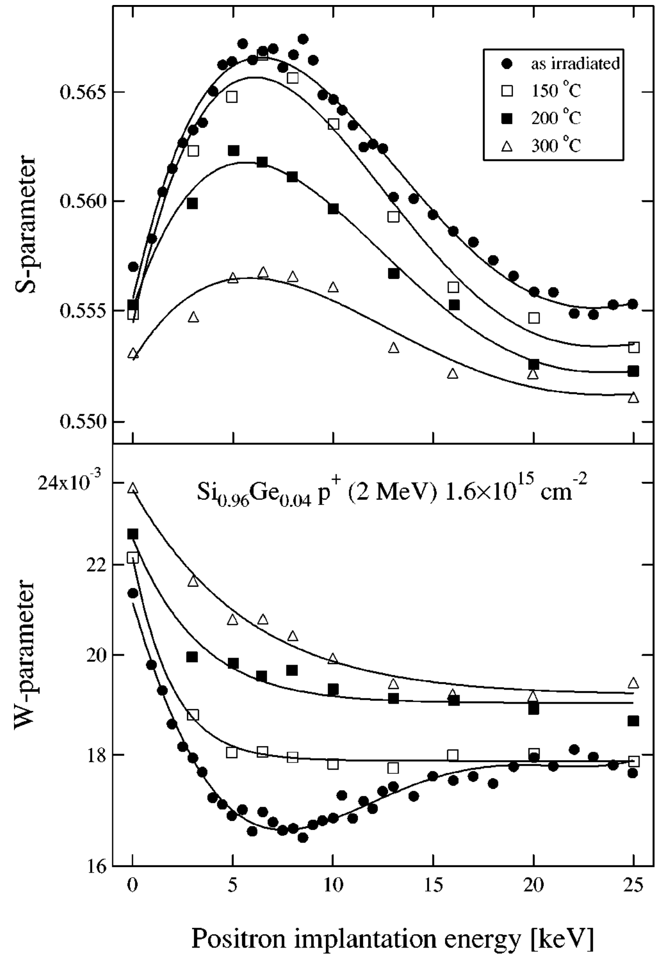

FIG. 5. S and W parameters as a function of positron implantation energy for the 30 min isochronal annealing of the $Si_{0.96}Ge_{0.04}$ sample irradiated with a proton dose of 1.6×10^{15} cm^{-2}. The solid lines are guides to the eye.

The (S,W) plot of the isothermal annealing is shown in Fig. 7. Only the full curves for the sample before annealing and after the last annealing are shown. The sharp turning points for the intermediate annealings are indicated in the figure, as well as the surface and substrate parameter. The turning points in the SiGe layer gradually move with increasing annealing time along a line from the characteristic (S, W) point of the V-P pair until they saturate at $(S,W)=(0.563,19.3\times10^{-3})$. This point characterizes positron annihilation at a new defect formed in the annealings.

Notice that careful attention was kept on the behavior of the surface parameter during the annealing series. By comparing the turning points in Fig. 7 with the respective surface points, it is evident that there is no correlation between the movement of these two points in the (S, W) plane during the annealing series, i.e., the surface does not influence the position of the turning point.

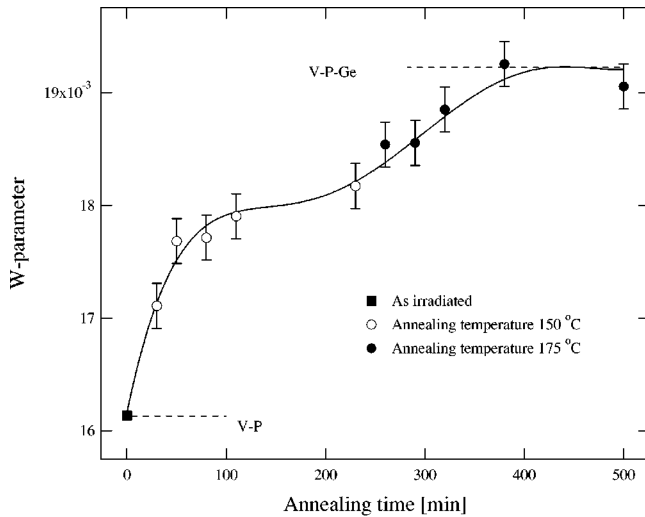

FIG. 6. The change in the W parameter (turning point 8–10 keV) plotted as a function of annealing time for the $Si_{0.96}Ge_{0.04}$ sample irradiated with a proton dose of 1.6×10^{15} cm^{-2}. The solid line is a guide to the eye. The dashed lines are the assigned characteristic V-P and V-P-Ge W/W_B parameter values obtained from the measurements.

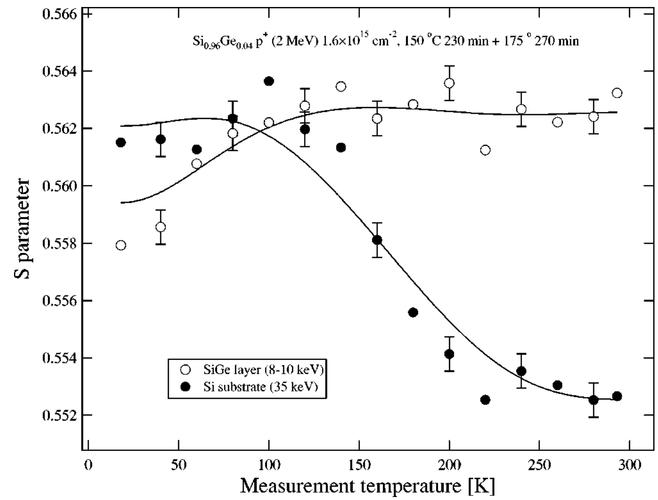

FIG. 8. S parameter values for the $Si_{0.96}Ge_{0.04}$ sample, proton dose 1.6×10^{15} cm^{-2}, after the isothermal annealing series as a function of measurement temperature. The solid lines are guides to the eye.

The sharp turning point in the S-W plot during the isothermal annealing procedure suggest that all positrons in the $Si_{0.96}Ge_{0.04}$ layer annihilate in vacancy complexes. To confirm this, the S and W parameters for the layer were measured as a function of temperature after the last annealing, the result for the S parameter is shown in Fig. 8. The temperature behavior of the S parameter curve is similar to that shown in Fig. 2(b). From these two facts, (i) the sharp turning point in the (S, W) plane and (ii) the lack of temperature dependence for the trapping of positrons, we come to the conclusion that all positrons annihilate in vacancy complexes in the SiGe layer and that the concentration of vacancy complexes in the as-irradiated sample and in the sample annealed isothermally are thus approximately equal, $\sim10^{18}$ cm^{-3}. However, the vacancy-type defect after annealing is not the simple V-P pair because its characteristic (S,W) parameters change in the annealings (Figs. 6 and 7).

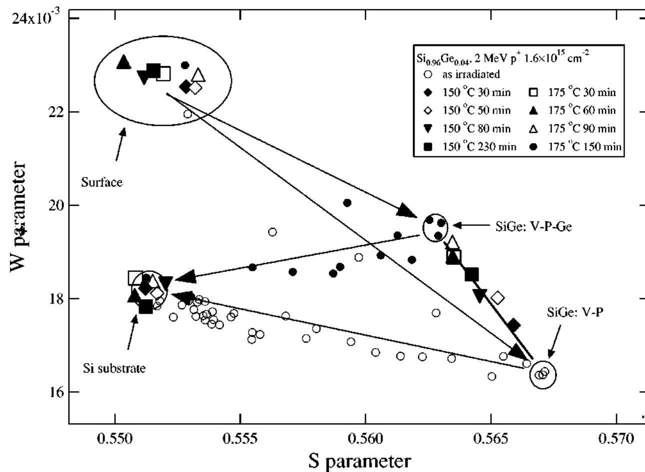

FIG. 7. S-W plot for the isothermal annealing of the irradiated $Si_{0.96}Ge_{0.04}$ sample, proton dose 1.6×10^{15} cm^{-2}. Only the full curves for the as irradiated and the last annealing are shown. Indicated in the figure are the surface and substrate points and the turning points for the intermediate annealings. The arrows indicate the direction of the increasing positron implantation energy, the turning points correspond to a positron implantation energy of 8–10 keV.

It can be noted that another interpretation of Fig. 8, i.e., that S parameter does not change with temperature, is that the vacancy-type defect could be in a neutral charge state. However, from DLTS studies of strained SiGe irradiated with protons we know that the samples are still n-type after irradiation and that the E centers are in the negative charge state after annealing in the temperature interval 150–200 °C.[8]

B. Formation of V-P-Ge complexes as the annealing product of V-P

To identify the defect formed in the annealings, we performed core electron momentum measurements with the coincidence technique. From the momentum curves in Fig. 9, we can observe that the intensity in the momentum distribution at high momenta ($>10\times10^{-3}m_0c$) is increasing with increasing annealing time. An increase in intensity in the high-momentum region means more positron annihilation with core electrons. Since we have saturation trapping through the whole annealing series, this is a clear implication that the surroundings of the vacancy that trap positrons is changing. The evident conclusion is that more positrons annihilate with germanium core electrons. The shape of the momentum distribution from $3d$ electrons in germanium, which are the outermost core electrons, is quite similar to that of $2p$ electrons in silicon,[14] and no changes of the slopes in Fig. 9 are thus expected due to germanium. Furthermore, the magnitude of W/W_B, Table II, correspond well to previ-

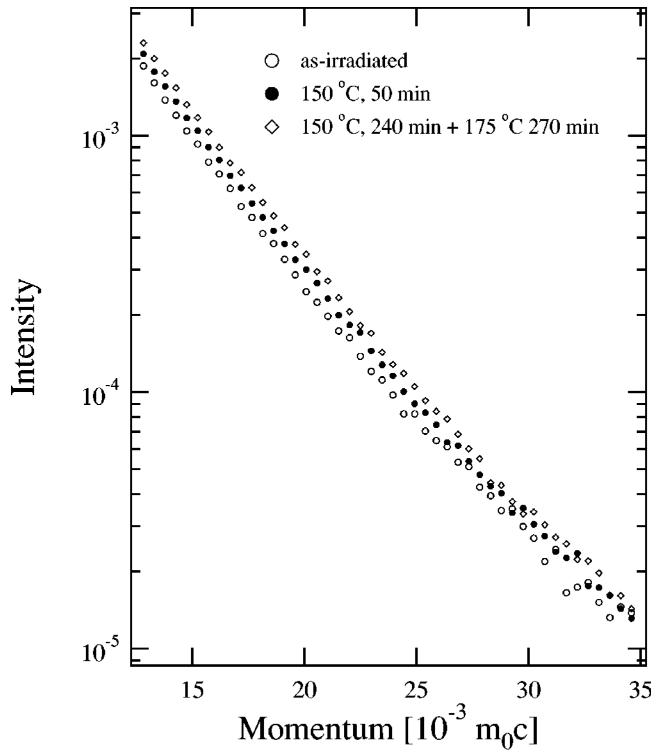

FIG. 9. Core electron annihilation measurements for the isothermal annealing of the the irradiated $Si_{0.96}Ge_{0.04}$ sample, proton dose 1.6×10^{15} cm^{-2}.

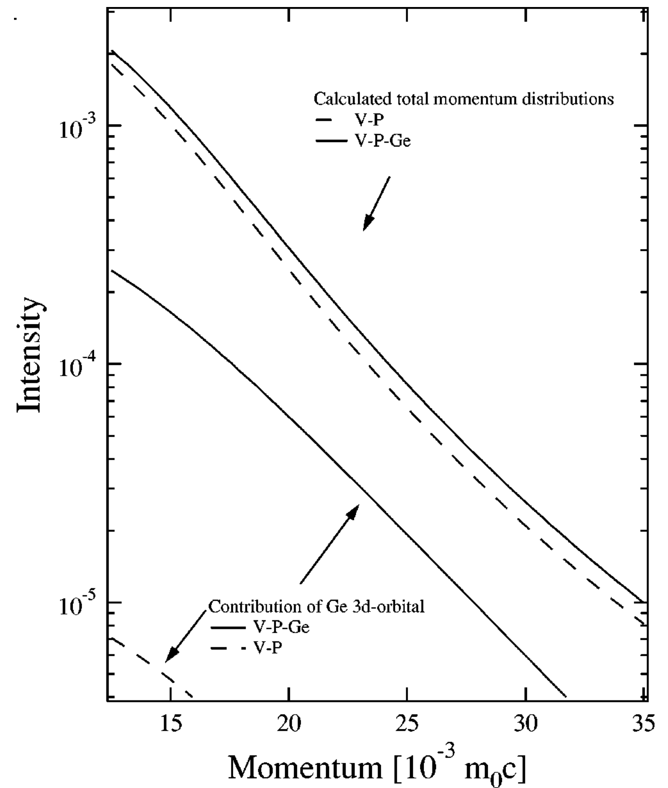

FIG. 10. Calculated core electron momentum curves for the V-P and the V-P-Ge complexs. The contribution of the Ge $3d$ orbital is also indicated in the figure.

ous results for the V-As pair in silicon,[17] where an arsenic atom (with the same outermost $3d$ core electron as in Ge) replaces one silicon atom in the surroundings of the vacancy. Hence, we conclude that a single germanium atom replaces a silicon atom in the surroundings of the vacancy as result of the annealing. The new vacancy-type defect is thus the V-P-Ge complex.

The same conclusion is reached by applying quantitative calculations. As can be seen from the calculated momentum distributions in Fig. 10, the increase in intensity is due to the germanium $3d$ electrons. The W parameters from the measured and calculated momentum distributions are summarized in Table II. The match between the experimental and calculated values are good. The comparison of the experimental results with calculations thus confirms that the new vacancy-type defect is a complex consisting of a vacancy, a phosphorus dopant, and a germanium atom.

DLTS studies made in Ref. 8 have suggested that the dominant defect in as-irradiated strained $Si_{0.96}Ge_{0.04}$(P) layers is the E center (V-P pair). The study further showed that this complex anneals at 100–200 °C leaving the divacancy as the dominant defect. By comparing the results for P doped strained SiGe and Sb doped relaxed SiGe,[25] it is suggested in Ref. 8 that the V-P-Ge is more stable than the V-P pair. This has been attributed to the fact that the P dopant causes the silicon lattice to contract and the Ge atom causes an expansion of the lattice. However, in the study of Monakhov *et al.*,[8] the V-P-Ge complex is not observed, perhaps because it is mixed in the divacancy DLTS peak due to the low P concentration ($\sim10^{17}$).

The higher annealing temperature of the V-P-Ge complex in SiGe is also supported by observations in pure silicon. Watkins has reported that a vacancy-germanium pair in silicon has a 30–60 °C higher annealing temperature than the isolated monovacancy.[26] This corresponds well with our observations for the V-P and V-P-Ge complexes, which give a 50 °C higher annealing temperature for the V-P-Ge complex.

In the present study, we do not observe any significant amount of V-P-Ge complexes in the as irradiated samples, however, we do observe V-P-Ge complexes when the samples are annealed in the temperature interval 150–175 °C. As mentioned in the preceding section, we observe saturation trapping of positrons to vacancy-type defects in the $Si_{0.96}Ge_{0.04}$ layer irradiated with 1.6×10^{15} cm^{-2} protons both for the as-irradiated case and for the isothermally annealed sample. Consequently, the defect concentrations in the as-irradiated case and in the isothermally annealed case are approximately equal, $\sim10^{18}$ cm^{-3}. From this we can conclude that the V-P-Ge complex is formed in the annealing procedure (150-175 °C), since statistically their concentration should be much lower in $Si_{1-x}Ge_x$, where x is only 4%.

A possible formation mechanism could be a migration process with the ring mechanism, which has been proposed for As diffusion in silicon.[27,28] In this mechanism, the vacancy makes a round trip in the hexagons of the ⟨110⟩ plane, i.e., it travels to the third nearest-neighbor site from the dop-

ant, before it again encounters the dopant and concludes a diffusion jump for the V-As pair. With this migration process the V-P pair could migrate as a pair until it encounters a germanium atom forming the V-P-Ge complex. This would explain the full conversion of V-P into V-P-Ge. Even if the V-P pair dissociated the independent diffusion of the vacancy and the P dopant could eventually lead to a stable V-P-Ge complex when both encounter the same Ge atom. However, recent calculations have shown that the correlated migration process of the E center is energetically more favorable,[28] because of the Coulombic interaction between the vacancy and the dopant.

Recently, Ranki *et al.*[5] observed that the E center in highly As doped silicon ($[\mathrm{As}]=10^{20}\ \mathrm{cm}^{-3}$) undergo a migration process where the migrating E center (V-As) first encounters a second arsenic dopant and forms the V-As_2 complex. This complex is also mobile and stabilizes when it encounters a third As dopant and forms the V-As_3 complex. A similar process could be possible in SiGe, however, the P concentration in the present samples is too low for V-P_2 complexes to form, i.e., the probability for the migrating E center to encounter a second P dopant is too small as observed previously for V-As.[5] Another possibility is the formation of V-P-Ge_2 complexes, since the concentration of Ge is certainly high enough to make this possible. A significant difference when comparing to As in silicon is that the V-As_2 can migrate as a complex since there is a Coulombic attraction between the negative vacancy and the positively charged dopants. Obviously there is no such attraction between the E center and the Ge atom in SiGe and it is therefore unlikely that the V-P-Ge complex could migrate as an entity. This is consistent with the lower annealing temperature of 200 °C for the V-P-Ge complex compared to 400–500 °C for the V-As_2 complex.

V. THE BINDING ENERGY OF *V*-P AND GERMANIUM

The experimental results show that the V-P pair becomes more stable when the vacancy is neighbored by a germanium atom. To estimate the difference in the binding energy, we describe the dissociations of the complexes V-P and V-P-Ge with an Arrhenius-type equation

$$N=\nu_0 t e^{-E/k_B T}, \tag{4}$$

where N is the number of jumps in time t, ν_0 is the Debye frequency, $E=E_B+E_M$ is the sum of binding and migration energies, k_B is the Boltzmann constant, and T is the temperature.

The V-P becomes mobile at 150 °C, which is taken as the dissociation temperature of this complex. This should be a reasonable estimate, since the binding energy between the vacancy and the P dopant at the third nearest-neighbor position in the ring mechanism should be small compared to the dissociation energy of the E center. The dissociation temperature of the V-P-Ge is 200 °C. In order to disappear in the positron experiment, the vacancy must travel roughly 500 nm in the 1 μm $Si_{1-x}Ge_x$ layer, i.e., $N=10^3-10^4$ jumps. With $t\sim1000$ s and $\nu_0\sim10^{13}\ \mathrm{s}^{-1}$, we obtain that the temperature interval of $\Delta T\sim50$ K, in which the V-P-Ge complex is seen in the experiment, corresponds to the energy difference of $\Delta E\sim0.13$ eV. In this experimental estimate we assume that the migration energy (E_M) is approximately equal for the two dissociation processes.

We have estimated the binding energy E_B of a vacancy-phosphorus complex theoretically using standard plane-wave pseudopotential method and a 64-atom simple cubic silicon supercell containing a V-P complex and a single Ge atom.[29] Three configurations were considered, one for the bound V-P-Ge complex (c) and two different configurations (a, b) for Ge separated from V-P as far as allowed by the 64-atom supercell. The differences in the calculated total energies $E_B\sim E_{a(b)}-E_c$ are 0.12 (0.20) eV for a charge neutral and 0.21 (0.28) eV for a singly negative supercell.[30] The calculations thus show that V-P-Ge is by 0.1–0.2 eV more stable than V-P, which is in very good agreement with the experimental binding energy.

Previous calculations for a vacancy in $Si_{0.5}Ge_{0.5}$ give that each additional Ge neighbor reduces the formation energy of the vacancy by 0.20–0.25 eV.[10,9] Boguslawski and Bernholc[9] have suggested that this is a direct consequence of the energies of the dangling bonds in the creation of the vacancy. The more extended Ge dangling bond leads to larger overlap for the unpaired electrons and thus lower orbital energy of the pairing orbitals in the vacancy.[10] As expected, our present calculations show the same effect for the V-P complexes in $Si_{0.96}Ge_{0.04}$. The result can be summarized by stating that each germanium dangling bond is energetically favored compared to that of silicon by roughly 0.20 eV. This simple intrinsic property of the Ge dangling bond gives a natural explanation to the experimental observations of the stability of the vacancy-phosphorus pair in n-doped $Si_{1-x}Ge_x$.

VI. CONCLUSIONS

We have used positron annihilation spectroscopy to identify and study the annealing behavior of vacancy-type defects in proton irradiated strained SiGe layers. We find that the dominating defect in the as-irradiated samples is the E center, a complex consisting of a vacancy and a phosphorus dopant. In the sample irradiated with the highest proton dose ($1.6\times10^{15}\ \mathrm{cm}^{-2}$) all positrons implanted in the SiGe layer are trapped and annihilate in the V-P pairs.

The isochronal and isothermal annealings show that a new type of defect is formed in the temperature interval 150–200 °C. The defect is identified as a complex consisting of a vacancy, a phosphorus dopant, and a germanium atom. Further investigation show that the concentration of vacancy-type defects in the as-irradiated and annealed samples are approximately equal. Hence, we conclude that the V-P-Ge complex is formed when a V-P complex migrating as a pair encounters a germanium atom and forms the V-P-Ge com-

plex, which is more stable than the V-P pair. The V-P-Ge complex anneals out at 200 °C. The 50 °C higher annealing temperature of the V-P-Ge complex corresponds to about 0.1–0.2 eV larger binding energy than that of the V-P pair. By *ab initio* calculations, we reproduce this value and confirm that the V-P pair is more stable when neighbored by a germanium atom.

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